Tuning the Electronic Properties of Semiconductor Colloids for Photochemical Energy Conversion

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Researchers in the Chemistry Division, Argonne National Laboratory have discovered a new phenomenon where the electronic band gaps, and hence the optical absorption of nano-sized semiconductor metal oxide colloids, are systematically tuned through chemical modification of the nanoparticle surface with a series of simple enediol organic ligands (figure 1). This finding is significant since it provides an elegant, new method for tuning the electronic properties of semiconductor nanoparticles for photochemical energy conversion applications. Semiconductor colloids have been intensively studied world-wide for possible applications in photovoltaic devices and photochemical energy conversion. A major impediment preventing effective utilization of metal oxide semiconductor photocatalysts has been the large electronic band-gap, and resulting poor optical absorption of metal oxide materials, such as TiO₂ which are widely investigated for possible application in photochemical energy conversion. The Argonne discovery has provided a solution to this problem by providing a mechanism for shifting the band gap of typical metal oxide colloids from the UV to the red edge (> 600 nm) of the solar spectrum. This shift allows the photochemistry of metal oxide colloids to be activated with light throughout the visible solar spectrum, and not just with UV light as is required for unmodified metal oxide materials. The Argonne researchers have shown that shifting of the electron band gap occurs because of ligand induced restructuring of surface defect sites, and that the ligands serve as "conductive" leads for attaching redox active molecules to the semiconductor particles. This discovery is expected to have a significant impact in a broad range of fields, including in the development of more efficient photovoltaic devices and the development of hybrid chemical systems for photochemical energy conversion.



Figure 1. 4.5 nm TiO_2 nanoparticles surface-modified with different enediol molecules: (1) bare TiO_2 , (2) salicylic acid, (3) dihydroxy-cyclobutenedione, (4) vitamin C, (5) alizarin, (6) dopamine, (7) t-butyl-cathecol.